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Magnetic properties of Nd_2CuO_4-type R_2CuO_4 (R = Y, Dy, Ho, Er, Tm) synthesized under high pressure: Weak ferromagnetism of Y_2CuO_4

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Magnetization of R_2CuO_4 (R=Y, Dy, Ho, Er, Tm) crystallizing in the Nd_2CuO_4-type (T') structure has been measured between 4 and 300 K. In Y_2CuO_4 antiferromagnetic ordering of Cu^{2+} spins at 260 K has been detected clearly, without being interfered with by the paramagnetic contribution of rare-earth elements as in the other compositions. Weak ferromagnetic behavior with a moment of 9×10^{-4} μ_B/Cu accompanies the antiferromagnetic transition. Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} ions obey the Curie-Weiss law at relatively high temperatures, and the effective moments are in good agreement with the values anticipated from their lowest multiplet levels. Various types of deviations from the law occur at low temperatures. Specifically, a sharp kink possibly suggesting antiferromagnetic ordering of the Dy^{3+} moments has been found at 7 K. Anomalies around 200 K for Ho_2CuO_4 and Er_2CuO_4 reflect the weak ferromagnetic contribution of the CuO_2 lattice.

INTRODUCTION

Since the discovery of high-temperature superconductivity in Cu oxides, much attention has been focused on the potential relevance of the antiferromagnetic character of two-dimensional Cu-O sheets to superconductivity. Magnetic properties of the prototype materials like La_2CuO_4 and Nd_2CuO_4 have been studied in detail.[1-3]

La_2CuO_4 and Nd_2CuO_4 crystallize in the so-called T and T' structures, respectively. In a previous paper we reported that R_2CuO_4's with R=Y, Dy, Ho, Er, and Tm are stabilized in the T' structure under high pressures,[4] while, under ambient pressure, only those with larger R ions, Pr-Gd, crystallize in this structure. Here we report preliminary results of magnetic measurements on these new T' phases. Especially Y_2CuO_4 has given an opportunity to reveal the magnetism of the CuO_2 sheets without being strongly interfered with by the rare-earth moments as in the other compositions.

EXPERIMENT

The samples were synthesized by the reaction of R_2O_3 and $R_2Cu_2O_5$ under a pressure of 6 GPa at 1223 K for 0.5 h using a belt-type apparatus (see Ref. 4 for further details). Magnetic measurements were made with a superconducting quantum interference device (SQUID) susceptometer between 4 and 300 K in applied fields of 0.01 and 0.1 T. The data were corrected for ionic diamagnetism of -16×10^{-6} emu/mole for O^{2-}, -11×10^{-6} emu/mole for Cu^{2+}, and -20×10^{-6} emu/mole for R^{3+}.[5]

RESULTS AND DISCUSSION

A. Y_2CuO_4

Figure 1 shows the temperature and field dependence of magnetization divided by applied field M/H of Y_2CuO_4. If the sample is cooled in zero field, magnetization measured on heating exhibits a broad maximum centered around 150 K as seen in curves a and b. It is apparent in these curves that magnetization is not linear to the magnitude of the external field. On field-cooling, however, magnetization tends to be saturated at low temperatures as seen in curve c.

Y^{3+} having no magnetic moment, these data have been

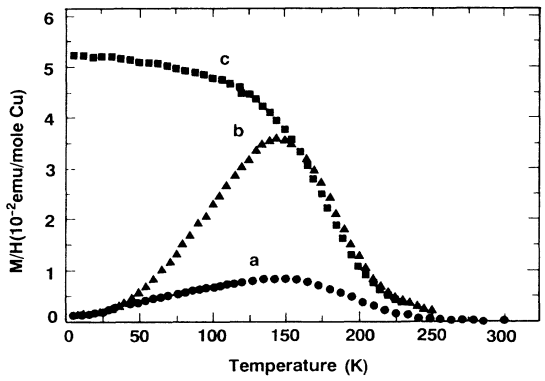

FIG. 1. M/H vs T (magnetization/field vs temperature) curves for Y_2CuO_4. Curve a, measured on heating with H=0.1 T; curves b and c, measured on heating and cooling, respectively, with H=0.01 T.

interpreted to directly point to the antiferromagnetic nature of the CuO_2 lattice accompanied by spin-canted weak ferromagnetism. From the temperature below which the M/H nonlinearlity appears, the Néel temperature has been determined to be ~260 K. The saturation magnetization measured on field-cooling down to 4 K corresponds to a ferromagnetic moment of 9×10^{-4} μ_B/Cu. If the Cu^{2+} ions are assumed to have an atomic moment of $0.5\mu_B$ as in Nd_2CuO_4,[3] the canting angle is calculated to be 0.05°.

The broad maximum in curves *a* and *b* in Fig. 1 has been interpreted to result from a competition between the magnetic anisotropy that fixes the spin axis along a certain crystalline direction and the energy gain attained by orienting the weak ferromagnetic moment along the applied field. If the anisotropy is dominant at low temperatures but is weakened more quickly as temperature rises, than the energy gain magnetization should show a broad peak on heating for a powdered sample. Even at a small field of 0.01 T, the anisotropy effect is almost negligible above 155 K.

The appearance of the weak ferromagnetic moment suggests a structural distortion of the CuO_2 lattice from tetragonal symmetry giving rise to antisymmetric exchange interactions between the Cu spins.[6] Such a distortion has been stated to be experimentally found for Nd_2CuO_4 at 300 K in Ref. 7, while it has been denied in Ref. 8. Careful x-ray diffraction measurements on Y_2CuO_4 are in progress.

From detailed magnetization measurements on Gd_2CuO_4 crystals Thompson *et al.*[9] suggested the possibility of a weak ferromagnetic nature of the CuO_2 lattice with a moment of $1.8\times10^{-3}\pm1.8\times10^{-3}$ μ_B/Cu (T_N=260 K), which is to be compared with the present data of 9×10^{-4} μ_B/Cu for Y_2CuO_4. According to a neutron-diffraction study of Nd_2CuO_4,[3] T_N is 255 K. Thus, T_N seems to remain almost constant for rare-earth compositions ranging over Nd–Y, though the intralayer Cu–O bond length is considerably shortened from 0.394 nm for R=Nd to 0.386 nm for R=Y.[4] This apparently suggests the importance of the interlayer interaction in setting T_N, but the interlayer distance is also considerably shortened from 1.217 nm for R=Nd to 1.170 nm for R=Y.[4]

It would be interesting to study Ce-for-Y substitution effects to find how injection of electrons into the CuO_2 lattice,[10] if done, varies the magnetism of this material; again magnetic measurements are expected to directly reveal the behavior of the CuO_2 lattice.

B. R_2CuO_4 with R=Dy, Er, Ho, and Tm

The temperature dependences of M/H and its reciprocal for R_2CuO_4 with R=Dy, Er, Ho, and Tm are shown in Figs. 2–5. In comparison with the data for Y_2CuO_4, it is apparent that the paramagnetic contribution of these rare-earth ions is roughly by an order of magnitude larger than the weak ferromagnetic contribution of Cu ions. Magnetization divided by applied field of these samples seems to follow the Curie-Weiss law, $\chi=M/H=C/(T-\theta)$, above 110, 210, 200, and 150 K, respectively. The rare-earth moment, $\mu=(3kC/N)^{1/2}$, and the para-

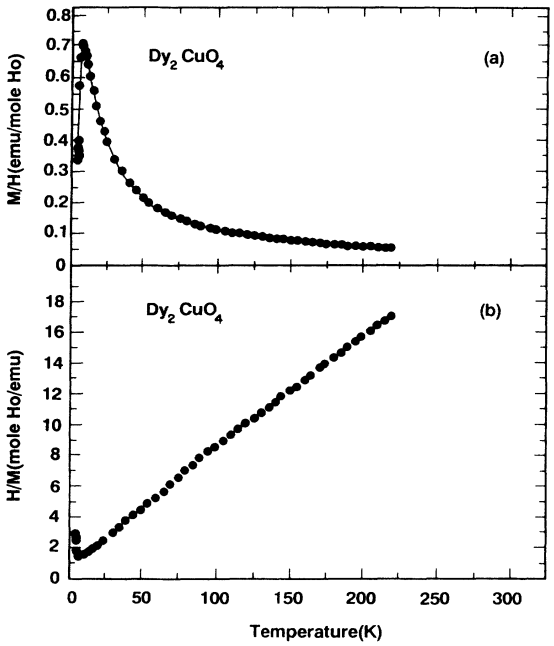

FIG. 2. (a) M/H and (b) its reciprocal measured on cooling with H=0.01 T for Dy_2CuO_4.

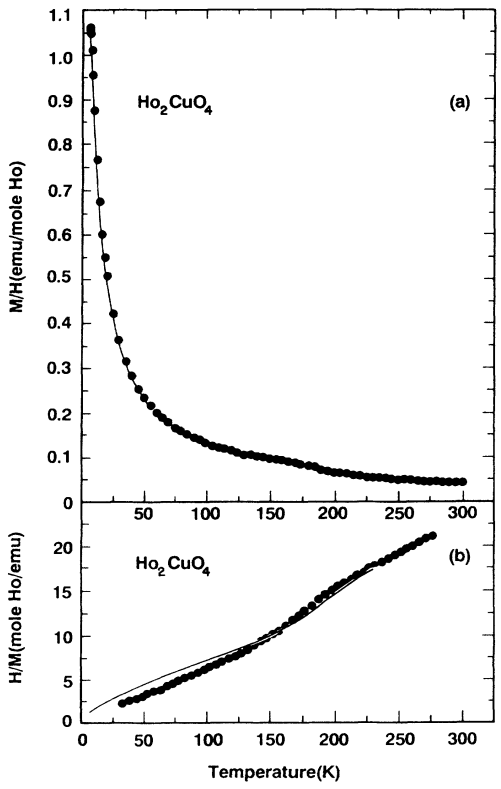

FIG. 3. M/H measured on heating at (a) H=0.01 T after zero-field cooling and (b) its reciprocal measured on cooling with H=0.01 T for Ho_2CuO_4. The solid line in (b) is a sum of the paramagnetic contribution of Ho^{3+} calculated using the parameters given in Table I and the field-cooled data for Y_2CuO_4 plotted in Fig. 1, curve *c*.

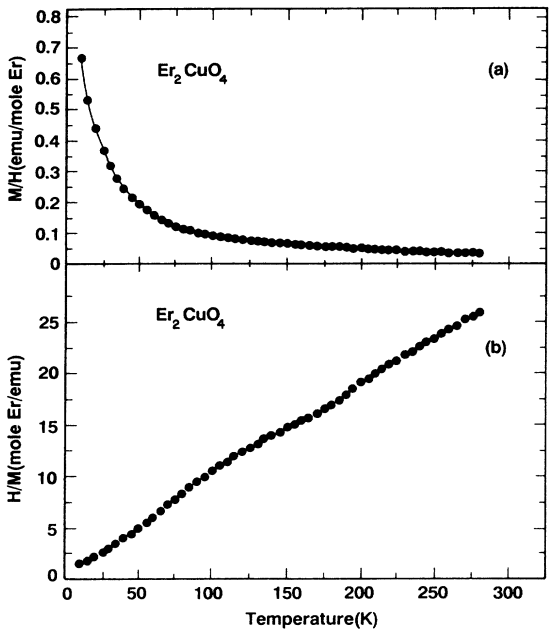

FIG. 4. (a) M/H and (b) its reciprocal measured on cooling with $H=0.01$ T for Er_2CuO_4.

magnetic Curie temperature θ evaluated from the linear relation of χ^{-1} vs T at high temperatures are summarized in Table I. For comparison the theoretical values of $\mu_J=g\mu_B[J(J+1)]^{1/2}$, where $g=1+[J(J+1)+S(S+1)-L(L+1)]/2J(J+1)$, for these R ions in their lowest multiplet levels are also listed in Table I. The experimental values agree with the calculated moments within 2%.

Deviations from the Curie-Weiss law at low temperatures have been reported for various phases with $R=$Pr-Gd. Influences of crystal-field splitting of the

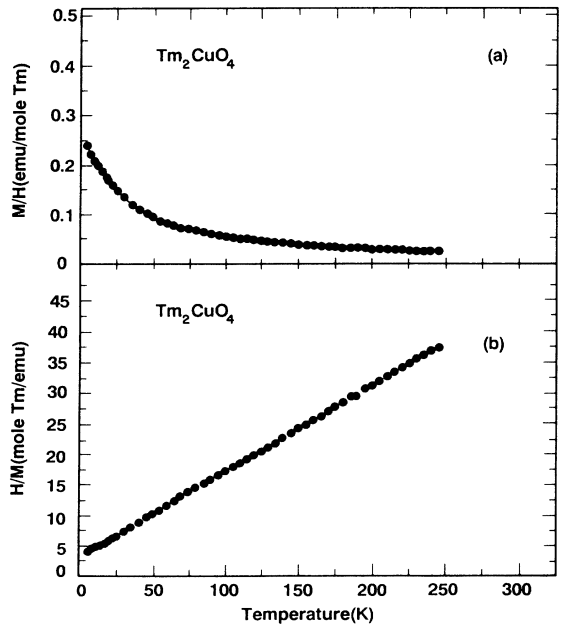

FIG. 5. (a) M/H and (b) its reciprocal measured on cooling with $H=0.01$ T for Tm_2CuO_4.

TABLE I. Calculated (μ_J) and experimental (μ and θ) magnetic parameters for R_2CuO_4 compounds.

Compound	μ_J/μ_B	μ/μ_B	θ (K)
Dy_2CuO_4	10.64	10.60	−22.1
Ho_2CuO_4	10.60	10.43	−12.2
Er_2CuO_4	9.58	9.64	−23.9
Tm_2CuO_4	7.56	7.49	−20.6

multiplet have been considered for $R=$Pr, Nd, Eu, and Sm by Saez-Puche *et al.*,[11] and influences of an internal field from the CuO_2 lattice has been detected for Gd_2CuO_4 around its T_N.[9] In addition, anomalies due to uncertain, e.g., Gd-Cu and/or Cu-Cu, interactions and antiferromagnetic order of Gd moments have been found at 20 and 6.5 K, respectively, for this material.[9]

The anomaly at 7 K for Dy_2CuO_4 seen in Fig. 2 is very similar in appearance to the sharp peak of an uncertain origin for Gd_2CuO_4 at 20 K, while the temperature of the anomaly, 7 K, is near the ordering temperature, 6.5 K, of the Gd moment and also near the temperature of 8 K where antiferromagnetic ordering of Nd moments in Nd_2CuO_4 has been speculated to occur.[3] Moreover, the sharp anomaly at 20 K for Gd_2CuO_4 appearing at 10^{-4} T has been reported to "move to lower temperatures with increasing field and merge with the anomaly associated with Néel ordering of gadlinium for fields greater than 5 kG." Thus, the origin of the 7-K anomaly may possibly be due to antiferromagnetic ordering of the Dy moment.

The deviation for Ho_2CuO_4 below ~200 K can be assigned to the weak ferromagnetic contribution of the CuO_2 lattice: Magnetization shows such a hysteresis as found in Y_2CuO_4. The M/H curve measured on heating after zero-field cooling [Fig. 3(a)] shows a broad anomaly around 150 K, and the data measured on field-cooling can be reproduced rather well [Fig. 3(b)] by assuming that the paramagnetic contribution of Ho^{3+} ions calculated using the parameters given in Table I is simply added to the field-cooling curve for Y_2CuO_4 plotted in Fig. 1(c). This kind of hysteresis has been detected also for Er_2CuO_4, though less pronounced. But it has not been found within experimental error for Dy_2CuO_4 nor for Tm_2CuO_4, though the absence of the anomaly does not mean disorder of the Cu moment.

In summary, this paper reports the magnetic properties of R_2CuO_4 with $R=$Y, Dy, Ho, and Tm stabilized in the T' structure under high pressure. Antiferromagnetism accompanied by a weak ferromagnetic moment was clearly detected for Y_2CuO_4 and Ho_2CuO_4. Antiferromagnetic ordering of Dy^{3+} moments has been suggested to take place at 7 K.

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